



Memorandum

From: Michael P. Lenkauskas

Date: September 20, 2013

Subject: EMSL Analytical (Libby, MT) Issues and Concerns

The following is a summary of issues and analytical data discrepancies associated with the EMSL Analytical laboratory in Libby, Montana. The discrepancies, identified by CDM Smith and CB&I, raise concerns about the quality of the data provided by this laboratory for samples collected from Operable Unit 3 (OU3) of the Libby Superfund Site. The specific issues include:

- TEM Inter-lab sample preparation issues
- Inadequate frequency of project-specific QC analyses
- Possible misidentification of samples
- Result discrepancies between TEM rapid TAT and full analysis of OU3 water samples

TEM Inter-lab Sample Preparation Issues

The EMSL Analytical laboratory experienced an unusually high percentage (37%) of damaged grid openings (GOs) on re-preparations prepared for the 2010 and 2011 TEM inter-laboratory, which resulted in these samples having to be re-prepped again, slowing down what turned out to be an already laborious process. Upon identification of this issue on March 25, 2013, the laboratory was directed to investigate and apply the necessary correction actions prior to preparing the re-preparations for the 2012 TEM inter-laboratory study about to be initiated. The root cause of the damaged GOs, as determined by the laboratory, is described in the attached corrective action (CAR# 1303-1), was the following:

- Grid opening size, EMSL uses a custom made grid with an opening of 0.0130 sq. mm;
- Grid condition;
- Carbon coating thickness;
- Ash time; and
- Packaging and shipping.

In addition to using a grid with a smaller grid opening size (15x15 grids with a G.O.A. of 0.0064 sq. mm) the laboratory is now also pre-cleaning the grids and has adjusted the asher and carbon coating settings. Since none of the 11 samples re-prepped by the laboratory for the 2012 TEM inter-laboratory were received damaged, the corrective actions initiated by the laboratory appear to have resolved the issue.

It should also be noted that undissolved filter material has also been observed on EMSL grid preparations, which will be investigated on a laboratory-by-laboratory basis during the 2012 laboratory on-site audits.

Inadequate Frequency of Project-specific QC Analyses

A review of the QC analyses available in the OU3 database for samples analyzed in 2012 revealed that the frequency at which QC analyses were performed for both TEM and PLM analyses during this period was not in accordance with the criteria described in Laboratory Modification LB-000029D and SOP SRC-

Libby-03 (rev. 3) for TEM and PLM, respectively. The following table provides a summary of analyses performed, the required frequency, the number of QC analyses that should have been performed, and the actual number and percentage of QC analyses that were performed:

Method	QC Type	Sample Analyses	Required Frequency	Performed	Actual Frequency
TEM	LB	293	4%	7	2.4%
TEM	RS	293	1%	0	0%
TEM	RD	293	2.5%	3	1%
TEM	VA	293	1%	2	0.7%
TEM	RP	293	1%	5	1.7%
PLM	LDC	65	8%	1	1.5%
PLM	LDS	65	2%	3	4.6%

Although QC analyses were not performed at the required frequency on a project-specific basis (OU3), they were prepared at the required frequency for all of the operable units combined. This discrepancy was brought to the attention of EMSL Analytical Management on May 22, 2013, who performed an investigation and determined that separate QC logbooks were maintained up until June 25, 2012, at which time they were combined¹. Effective May 23, 2013 samples received from OU3 are once again recorded in a separate, OU3-specific, QC logbook, ensuring that project-specific QC will be performed at the required frequencies.

Possible Misidentification of Samples

A review of the results from surface water samples collected from OU3 during the spring of 2012 and analyzed by the laboratory indicates that samples were misidentified either in the field during collection or in the laboratory while being processed. Samples possibly misidentified are summarized in the following table:

Index ID	Sample Type	Date Prepared	Date Analyzed	Structures	Comments
P5-10013	Field Sample	5/09/12	5/25/12	0	Same preparation batch.
P5-10014	Field Blank		5/26/12	25	
P5-10067	Field Sample	6/20/12	6/26/12	25	Field sample/field duplicate pair
P5-10068	Field Duplicate		6/26/12	1	
P5-20018	Field Sample	5/17/12	6/01/12	0	Field sample/field duplicate pair. Lab RP had 50 structures.
P5-20019	Field Duplicate		6/02/12	65	
P5-20085	Field Sample	7/04/12	7/09/12	5	Field sample/field duplicate pair
P5-20087	Field Duplicate		7/09/12	27	
P5-20225	Field Sample	9/20/12	11/08/12	25	Field sample/field duplicate pair
P5-20226	Field Duplicate		11/08/12	62	

Although sometimes analyzed on separate days, each of the sample pairs in question were prepared on the same days by the same preparer, increasing the possibility that the misidentification of at least the field duplicate pairs at the laboratory. It should also be noted that with the exception of the sample pair prepared and analyzed in September and November, respectively, which has results that may or may not indicate the samples were misidentified, the remaining samples, which exhibit much greater disparity, were all prepared and analyzed during the spring/early summer 2012.

The potential that the misidentification of samples was brought to EMSL Analytical Management's attention, and on February 19, 2013 the laboratory provided a memo to both EPA and Remedium summarizing the findings of their investigation. The first section of this memo discusses the TEM Rapid TAT versus TEM full analysis discrepancies, which are discussed below. Concerning the possible misidentification of samples, the laboratory offered the explanation that at the time of the misidentifications the laboratory was operating beyond its capacity, creating a disorganized environment

¹ Note that this timeframe coincides with the change in the OU3 laboratory subcontracting mechanism from Remedium to TechLaw.

with staff trying to handle too many responsibilities. Procedural changes put in place by the laboratory to prevent similar situations for occurring in the future include:

- Expansion of the sample preparation area creating a less cluttered workspace in which to stage more samples in an organized manner
- Restricting the number of jobs being prepared simultaneously
- Having one individual track the progress of each individual lab job
- Provide training and improve intra-laboratory communication to better handle lab capacity issues

Note: Although this memorandum indicated that the capabilities of the Denver laboratory were to be increased to handle duff and water samples, as of the spring of 2013, this action has not been implemented.

Result discrepancies between TEM rapid TAT and full analysis of OU3 water samples

For a subset of the Kootenai River water samples collected in 2012, the EMSL-Libby laboratory was requested to perform a “rapid” TAT analysis. This analysis was performed using the same preparation techniques and counting rules as the traditional “full” analysis, but only required the analyst to record the total number of countable LA structures per GO (i.e., recording of structure-specific attributes, such as length, width, and structure type, was not required) to facilitate the faster reporting of water concentrations. Following the rapid TAT analysis, each water sample was subsequently re-analyzed² using the traditional full analysis reporting requirements.

A comparison of the rapid vs. full analysis results performed in January/February 2013 revealed significant discrepancies between the reported water concentrations for several samples (examples provided below):

Index ID	Total LA Water Conc. (MFL)	
	Rapid Analysis	Full Analysis
P5-10004	3.7	0
P5-10010	97	0
P5-10008	62	0
P5-10013	40	0

These discrepant results were brought to EMSL Analytical Management’s attention, and the laboratory repeated the rapid and full analysis for a subset of the Kootenai River water samples (from the raw water that was in archive) to identify the nature of these discrepancies. The results of these repeated analyses indicated that the reported water concentrations from the original rapid analysis were not confirmed, but that the original full analysis results were confirmed *for most samples*. On this basis, the laboratory provided a memo to both EPA and Remedium on February 19, 2013, recommending that “*all rapid results should be disregarded in favor of the full ISO analyses*”. This memo did not specify the reason for the differences between the rapid and full analysis results, but EMSL noted in a subsequent memo on September 4, 2013, that the analyst performing the rapid analysis erroneously utilized PCM recording rules, resulting in the recording of diatom fragments as countable structures.

However, as noted above, the repeat full analyses did not confirm the results for all samples. In particular, for a subset of samples, the repeat full analysis did not confirm either the original rapid analysis or the full analysis:

Index ID	Total LA Water Conc. (MFL)		
	Original Analysis		Repeat
	Rapid Analysis	Full Analysis	Full Analysis
P5-10018	78	35	0
P5-10017	37	58	0

² Because the grids from the rapid analysis were often blown due to the original examination, this re-analysis was performed using a newly prepared set of grids from the original filter.

Index ID	Total LA Water Conc. (MFL)		
	Original Analysis		Repeat
	Rapid Analysis	Full Analysis	Full Analysis
P5-10015	34	60	0

In the case of one field blank (P5-10014), the re-analysis supported the unexpected results of the original full analysis, which reported a total LA water concentration of about 25 MFL. Because of these discrepancies, the validity of the original full analysis results is also uncertain.

Resolution of discrepancies for OU3 water samples

Re-analyses of samples collected in 2012

As a consequence of the discrepancies discussed above, several re-analyses were performed of the water samples collected in 2012 from the Phase V Part A (Kootenai) and Part B (Ecological) studies to confirm the originally reported results. This re-analysis effort included the analysis of a subset of water samples from the Kootenai River study (i.e., samples collected during Rounds 1 through 5 from stations LRC-6 and UKR-0) and the in-stream fish toxicity tests (i.e., a subset of the LRC surface water samples from the eyed egg study and 20% of the surface water samples from the fry study). These re-analyses were performed by EMSL-Cinnaminson in July/August 2013 from the raw water³.

Table 1 (see below) summarizes these results. As shown, of the 25 samples that were re-analyzed, there were 9 samples where the re-preparation analysis performed by EMSL-Cinnaminson was statistically different from the original analysis performed by EMSL-Libby (based on a Poisson ratio comparison test at a 90% confidence interval). This means that the difference in LA water concentrations between the original analysis and the re-preparation analysis was more than can be attributed to Poisson counting error alone. For the 4 samples that were different from the Part A program (Kootenai), these results confirmed that some type of filter mix-up had occurred for samples P5-10014, P5-10015, P5-10017, and P5-10018 during the original analysis at EMSL-Libby. For sample P5-10014, the results confirmed that both the original analysis (reported in May 2012) and the re-analysis (performed in May 2013) by EMSL-Libby were in error. All of these samples were prepared by the same person on the same day (5/9/2012). This preparation batch included 16 samples (P5-10013 through P5-10027). Most of the samples in this preparation batch (P5-10019 through P5-10027) were associated with a pilot study to evaluate differences in three different water sampling methodologies and were not part of the Kootenai River sampling program.

For the other 5 samples that were different from the Part B program (Ecological), there appears to be a consistent bias, with EMSL-Cinnaminson reporting higher concentrations than EMSL-Libby. Although for most of these samples, the concentrations are usually within a factor of about 3, there was one sample (P5-20027) where the reported concentration by EMSL-Cinnaminson is about 90 times higher than what was reported by EMSL-Libby, which may indicate another potential filter mix-up.

Re-analyses of samples collected in 2013

In addition, approximately 20% of the water samples collected as part of the 2013 eyed egg study were also be randomly selected *a priori* for re-analysis by EMSL-Cinnaminson in July/August 2013. These re-analyses were performed from either the originally prepared filter or the raw water (depending upon the nature of the archived sample).

Table 2 (see below) summarizes these results. A total of 17 samples were selected for re-analysis by EMSL-Cinnaminson; 10 samples were re-prepared from the filter (filter was prepared by EMSL-Libby) and 7 samples were re-prepared from the raw water. As shown, 8 of the 17 samples that were re-analyzed by EMSL-Cinnaminson was statistically different from the original analysis performed by EMSL-Libby (based on a Poisson ratio comparison test at a 90% confidence interval). Similar to what was observed in

³ For two samples, the re-analysis was performed from the original filter because no raw water remained (these samples are indicated in the table).

the 2012 re-analyses, there appears to be a consistent bias, with concentrations reported by EMSL-Libby tending to be lower than those reported by EMSL-Cinnaminson. However, concentrations in most samples were usually within a factor of about 2.

Of particular interest are the results for samples P5-20325 and P5-20326. These two samples were preferentially selected for re-analysis because the originally reported LA concentrations suggested that the results for the pore water and its paired surface water got mixed up. The re-analysis performed by EMSL-Cinnaminson confirmed that a filter mix up did occur and that it happened in EMSL-Libby when reporting the results (not in the field)⁴.

Conclusions

The results of these re-analyses support the conclusion that filter mix-ups occurred at EMSL-Libby both in 2012 and 2013. The largest mix-up appears to be associated with the set of filters that were prepared during Round 3 of the Phase V, Part A (Kootenai) sampling effort (which included P5-10014, P5-10015, P5-10017, and P5-10018). However, other filter mix-ups outside of this timeframe were also noted, and even occurred during the 2013 study after corrective actions were to have been implemented.

The re-analyses also show that there are differences between the EMSL laboratories in the identification and recording of LA structures in water samples from OU3, albeit the magnitude of the differences in the reported water concentrations are not large (usually within a factor of 2-3).

Resolutions and Recommendations

Based on discussions with EPA, the following resolutions were reached with regard to the 2012/2013 water analyses:

- For samples where the re-analysis confirmed that a filter mix-up occurred (i.e., P5-10014, P5-10015, P5-10017, P5-10018, P5-20325, and P5-20326), the original EMSL-Libby results will be rejected; a corrected EDD will be submitted changing the *Filter Status* field from 'Analyzed' to 'Cancelled' and an analysis comment will be added regarding the rejected status. A modified EDD will be submitted for the corresponding EMSL-Cinnaminson analyses that will be used in preference; a corrected EDD will be submitted changing the *Lab QC Type* from 'Repreparation' to 'Not QC' and an analysis comment will be added explaining why the QC status was changed. The revised EDDs will be uploaded to the OU3 project database.
- For all other samples that were re-analyzed, the EMSL-Libby result will be retained as the 'Not QC' analysis and the EMSL-Cinnaminson result will be retained as the 'Repreparation'. When these results are summarized, the results of the repreparations will be used to demonstrate the between-laboratory differences in TEM counting and recording and results uncertainty/variability, but will not be used to alter the reported results.

For future OU3 investigations, the following recommendations were made:

- Ensure that SAP/QAPPs for 2014 water sampling at OU3 include a 20% repreparation requirement (from raw water) by EMSL-Cinnaminson.
- Ensure that a copy of the analytical summary sheet is included with all submitted chain of custody forms.
- Ensure that all analysts have access to the appropriate eRooms and are familiar with any site-specific methods and procedures prior to analysis.

⁴ As shown in the table, EMSL-Cinnaminson performed an extra repreparation analysis which confirmed their results for sample P5-20326.

Additionally, EPA's laboratory support contractor, Tech Law, Inc., was tasked with providing onsite re-training of all TEM analysts in the EMSL-Libby laboratory, developing a training procedure for all TEM laboratories, and preparing reference material standards (e.g., pyroxene, actinolite, tremolite) to minimize potential between-laboratory differences in LA structure reporting in future TEM analyses.

TABLE 1
LIBBY OU3: 2012 PHASE V, SURFACE WATER RE-ANALYSIS RESULTS
REPREPARATION RESULT COMPARISON

Investigation	Repreparation Type	Index ID	Original Analysis (2012)				Repreparation Analysis (Jul/Aug 2013, EMSL-Cinnaminson)				Poisson Rate Comparison (90% CI)
			Laboratory	Total LA Structures	Sensitivity (1/L)	Total LA Conc (MFL)	Laboratory	Total LA Structures	Sensitivity (1/L)	Total LA Conc (MFL)	
2012 Phase V Part A Surface Water	Raw water	P5-10005	EMSL27	2	3.3E+05	0.7	EMSL04	0	1.3E+06	0	[0-13.62] The rates are not different
	Raw water	P5-10006	EMSL27	121	3.5E+06	419	EMSL04	39	1.2E+07	473	[0.65-1.23] The rates are not different
	Raw water	P5-10011	EMSL27	0	1.6E+05	0	EMSL04	0	6.4E+05	0	Both counts are 0; the rates are not different
	Raw water	P5-10012	EMSL27	27	1.5E+06	42	EMSL04	25	1.9E+06	47	[0.54-1.46] The rates are not different
	Raw water	P5-10014	EMSL27	25	9.2E+05	23	EMSL04	0	2.6E+04	0	[0-0] Rate 1 is greater than Rate 2
	Filter	P5-10015	EMSL27	26	2.3E+06	60	EMSL04	0	1.8E+05	0	[0-0.01] Rate 1 is greater than Rate 2
	Raw water	P5-10017	EMSL27	25	2.3E+06	58	EMSL04	1	6.4E+05	0.6	[17.65-1828.91] Rate 1 is greater than Rate 2
	Raw water	P5-10018	EMSL27	25	1.4E+06	35	EMSL04	0	6.4E+05	0	[0-0.06] Rate 1 is greater than Rate 2
	Raw water	P5-10025	EMSL27	27	2.8E+06	75	EMSL04	26	1.9E+06	51	[0.91-2.42] The rates are not different
	Raw water	P5-10033	EMSL22	1	4.9E+04	0.05	EMSL04	3	2.8E+04	0.09	[0.02-5.24] The rates are not different
	Raw water	P5-10034	EMSL22	121	2.8E+05	33	EMSL04	114	2.7E+05	31	[0.87-1.36] The rates are not different
	Raw water	P5-10053	EMSL04	0	5.0E+04	0	EMSL04	1	2.1E+04	0.02	[0-44.2] The rates are not different
	Raw water	P5-10056	EMSL04	66	2.5E+05	16	EMSL04	84	2.4E+05	20	[0.6-1.05] The rates are not different
2012 Phase V Part B Eyed Egg Surface Water	Raw water	P5-20002	EMSL27	58	6.9E+05	40	EMSL04	26	1.6E+06	42	[0.63-1.46] The rates are not different
	Raw water	P5-20006	EMSL27	33	6.9E+05	23	EMSL04	26	8.1E+05	21	[0.68-1.74] The rates are not different
	Raw water	P5-20011	EMSL27	25	7.9E+04	2	EMSL04	25	2.6E+05	7	[0.18-0.5] Rate 1 is less than Rate 2
2012 Phase V Part B Fry Surface Water	Raw water	P5-20016	EMSL04	46	8.2E+05	38	EMSL04	60	8.2E+05	49	[0.54-1.08] The rates are not different
	Filter	P5-20018	EMSL04	0	8.5E+04	0	EMSL04	0	8.6E+04	0	Both counts are 0; the rates are not different
	Raw water	P5-20021	EMSL04	26	5.0E+05	13	EMSL04	25	5.5E+05	14	[0.58-1.58] The rates are not different
	Raw water	P5-20027	EMSL04	25	6.7E+04	2	EMSL04	60	2.4E+06	146	[0.01-0.02] Rate 1 is less than Rate 2
	Raw water	P5-20031	EMSL04	41	2.5E+05	10	EMSL04	73	2.4E+05	18	[0.4-0.79] Rate 1 is less than Rate 2
	Raw water	P5-20042	EMSL22	34	1.0E+06	34	EMSL04	39	9.7E+05	38	[0.59-1.35] The rates are not different
	Raw water	P5-20045	EMSL27	2	5.2E+04	0.1	EMSL04	3	5.1E+04	0.2	[0.08-4.34] The rates are not different
	Raw water	P5-20069	EMSL27	79	2.8E+05	22	EMSL04	42	9.7E+05	41	[0.39-0.75] Rate 1 is less than Rate 2
	Raw water	P5-20081	EMSL27	25	1.4E+05	3	EMSL04	31	7.8E+05	24	[0.09-0.23] Rate 1 is less than Rate 2

All filters pass the CHISQ test for filter loading evenness.

Notes:

LA - Libby amphibole

-- = result not available

L = liter

MFL - million fibers per liter

% = percent

CI = confidence interval

TEM = transmission electron microscopy

Original Analysis > Repreparation Analysis

Original Analysis < Repreparation Analysis

Repreparation analysis confirms suspected filter mix-up at the laboratory during the original analysis.

TABLE 2
LIBBY OU3: PHASE V PART B, 2013 EYED EGG STUDY, WATER SAMPLING RESULTS
REPREPARATION RESULT COMPARISON

Repreparation Type	Media Type	Index ID	Original Analysis (EMSL-Libby)			Repreparation Analysis (EMSL - Cinnaminson)			Poisson Rate Comparison (90% CI)
			Total LA Structures	Sensitivity (1/L)	Total LA Conc (MFL)	Total LA Structures	Sensitivity (1/L)	Total LA Conc (MFL)	
Reprep from filter	Surface Water	P5-20290	27	1.4E+06	38	25	9.8E+05	25	[0.96-2.57] The rates are not different
	Surface Water	P5-20294	27	1.2E+06	34	25	8.9E+05	22	[0.92-2.48] The rates are not different
	Pore Water	P5-20299	28	2.5E+06	70	50	2.5E+06	123	[0.37-0.86] Rate 1 is less than Rate 2
	Surface Water	P5-20300	0	1.2E+05	0	6	1.3E+05	0.8	[0-0.59] Rate 1 is less than Rate 2
	Surface Water	P5-20309	26	1.3E+06	35	25	2.5E+06	61	[0.34-0.93] Rate 1 is less than Rate 2
	Pore Water	P5-20336	1	8.3E+04	0.08	2	8.6E+04	0.2	[0.02-6.16] The rates are not different
	Pore Water	P5-20324	27	1.3E+06	36	37	1.3E+06	48	[0.47-1.16] The rates are not different
	Surface Water	P5-20325	26	1.7E+06	43	25	1.1E+05	2.6	[9.93-27.01] Rate 1 is greater than Rate 2
	Pore Water	P5-20326	0	7.8E+04	0	33	1.6E+06	54	[0-0] Rate 1 is less than Rate 2
						46	1.6E+06	75	[0-0] Rate 1 is less than Rate 2 **
	Surface Water	P5-20331	25	3.7E+05	9	25	6.5E+05	16	[0.34-0.94] Rate 1 is less than Rate 2
Reprep from water	Pore Water	P5-20338	34	1.7E+06	56	32	1.3E+06	41	[0.88-2.11] The rates are not different
	Surface Water	P5-20341	25	2.4E+05	6	25	2.5E+05	6	[0.57-1.58] The rates are not different
	Pore Water	P5-20348	30	1.7E+06	50	32	9.2E+05	30	[1.07-2.64] Rate 1 is greater than Rate 2
	Surface Water	P5-20356	25	7.1E+05	18	31	1.1E+06	33	[0.33-0.86] Rate 1 is less than Rate 2
	Pore Water	P5-20352	0	8.3E+04	0	3	8.5E+04	0.3	[0-1.67] The rates are not different
	Pore Water	P5-20363	0	1.3E+05	0	0	1.3E+05	0	Both counts are 0; the rates are not different
	Surface Water	P5-20369	0	1.2E+05	0	0	1.3E+05	0	Both counts are 0; the rates are not different

All filters pass the CHISQ test for filter loading evenness.

Notes:

LA - Libby amphibole

-- = result not available

L = liter

MFL - million fibers per liter

% = percent

CI = confidence interval

TEM = transmission electron microscopy

Original Analysis > Repreparation Analysis

Original Analysis < Repreparation Analysis

These samples were selected for repreparation analysis by EMSL-Cinnaminson because it was suspected that the paired pore water and surface water results were mixed up by EMSL-Libby. The filter repreparation results confirm that the results were reported incorrectly by EMSL-Libby.

****EMSL-Cinnaminson performed a second repreparation for this filter which confirmed the first repreparation.**